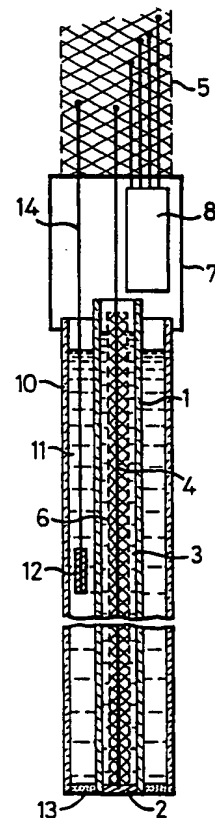




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(21) International Application Number: PCT/EP92/00769 (22) International Filing Date: 2 April 1992 (02.04.92) (30) Priority data: 9107036.7 4 April 1991 (04.04.91) GB (71) Applicant (for GB only): KODAK LIMITED [GB/GB]; Patent Department W92, Headstone Drive, Harrow HA1 4TY (GB). (71) Applicant (for all designated States except GB US): EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventors; and (75) Inventors/Applicants (for US only) : EDWARDS, Stephen, John [GB/GB]; 56 Marsworth Avenue, Pinner, Middlesex HA5 4TT (GB). FUGGLE, Graham, Anthony [GB/GB]; 76 Headstone Lane, North Harrow, Middlesex (GB).		(74) Agents: TRIBE, Thomas, Geoffrey et al.; F.J. Cleveland & Company, 40/43 Chancery Lane, London WC2A 1JQ (GB). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ELECTRODE CALIBRATION (57) Abstract An electro-analytical sensing instrument such as a pH meter has a sensing electrode which is placed in an electrolyte and voltages are read out in order to measure the properties of the electrolyte such as pH. The present invention enables an electrode assembly to be calibrated at one site and used at other sites and with other instruments without the need for re-calibration. This is achieved by providing a calibration unit including a memory which is kept as part of the electrode assembly for use at other sites. Various electrode assemblies to which the invention can be applied are described.		



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ELECTRODE CALIBRATION

5 This invention relates to electro-analytical
sensing instruments having sensor probe electrodes,
and is particularly concerned with the calibration and
use of the electrodes.

10 When measuring an active electrochemical species
potentiometrically, that is by measurement of the
voltage between electrodes in an electrolyte (the
analyte), it is first essential to calibrate the
instrument in standard solutions or buffers of known
activity to allow the slope and offset voltage to be
15 determined and used in subsequent measurements. These
values are either held by analogue potentiometers in
the measurement instrument circuits, or stored in
memory, if the instrument is digital. Once calibrated,
the measuring electrodes - either a separable
20 indicator electrode and reference electrode, or a
combined pair - cannot be disconnected from that
instrument and connected to another, perhaps in a
different area, without re-calibration.

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The present invention is concerned therefore with the problem of allowing the calibration and measurement of such sensors to be carried out at one site or in one instrument and used in another instrument or at another site.

The invention is further concerned with the problem of providing a device which can be used for any type of sensor which requires re-calibration.

It is known that the voltage measured when using a potentiometric electrochemical sensor is mainly dependant on the analyte, and is given by the following Nernst equation:

$$E(\text{measured}) = E_{(\text{indicator electrode half cell})} - E_{\text{ref}}$$

where

$$E_{(\text{indicator electrode half cell})} = E_{(\text{standard})}^{\circ} + \frac{RT}{nF} \cdot \ln(A_{\text{species}})$$

and

$$E_{\text{ref}} = E_{(\text{reference half cell})} + E_{(\text{junction potentials})}$$

A_{species} is the activity of species A and is approximately equal to the concentration of A in dilute solutions.

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In normal circumstances the reference half cell and junction potentials are not predictable to more than a few millivolts and may vary considerably between different reference electrodes. If it is
5 necessary to obtain a direct instrument read-out in either concentration or $\ln(\text{concentration})$ it is necessary to first convert from the millivolts measured by calibrating the system on a number of standard solutions. The difference between
10 theoretical millivolts and those measured is the offset voltage of that particular system. It is stored in the measuring instrument for later use, either by using a potentiometer to offset the millivolts measured back to the theoretical reading or
15 digitally by using a micro-processor and memory.

In a perfect system the millivolts measured are proportional to the logarithm of the activity of the analyte. From the Nernst equation this can be seen to
20 be:

$$(RT/nF) \cdot \ln(A_{\text{species}})$$

or

$$2.303 \cdot (RT/nF) \cdot \log(A_{\text{species}})$$

At a temperature of 25°C this is 59.13mV per
25 decade increase in concentration.

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In practice this theoretical factor is rarely obtained and an empirical factor calculated from the calibration data obtained by measuring standard solutions is used instead. This factor is obtained and stored for later use in an analogue instrument by setting the gain of the input circuits when measuring the standard solutions. In a micro-processor instrument this is stored directly as a factor in memory. This factor is defined as the slope of the system and may be presented as a percentage.

As stated above when measuring an active electrochemical species potentiometrically, it is first essential to calibrate in standard solutions or buffers of known activity to allow the slope and offset voltage to be determined and used in subsequent measurements.

According to the invention the calibration data is stored in a calibration unit in close physical association with the electrode or electrode pair assembly rather than in the broader confines of the instrument itself. This means that the electrode assembly and calibration unit can be disconnected from the instrument and taken to a remote site. A new

- 5 -

instrument can then read this information and be ready to measure without the need for re-calibration.

Accordingly the invention provides an electrode assembly for connection to an electro-analytical sensing instrument which comprises at least one measuring electrode and, associated with said electrode, a calibration unit including a memory means, which is arranged to store calibration data to enable the assembly to be used with more than one sensing instrument.

This approach means that one indicator and reference electrode pair can be calibrated in a laboratory or clean area and can then be taken into a factory environment, where buffer or standard solution might be contaminated, for solution measurements.

Preferably the assembly in accordance with the invention comprises a small memory and communications integrated circuit sealed into either electrode or probe or holder assembly together with a micro-processor instrument. The electrode pair can be calibrated in the normal process with buffers or standard solutions and the calibration data such as the slope and the offset voltage, can then be stored

- 6 -

in the memory means in the electrode pair via a serial communications link. This information may then be stored in non-volatile memory, for example in battery-backed RAM, EPROM or EEPROM for future use. The electrodes may then be disconnected, taken into a new area and connected to a different instrument. The new instrument will then retrieve this calibration data and be ready to carry out measurements.

Other information regarding time of calibration, safe time available before re-calibration is necessary, identification numbers and electrode type can also be stored.

The memory means is conveniently incorporated in the lead assembly of an existing electrode system.

The memory means may also include line drivers or impedance converters if the electrodes are of high impedance or the measuring instrument is likely to be located at a large distance from the electrodes.

The electrode assembly according to the invention may also be made intrinsically safe for areas where inflammable solvents are used. Calibration can then take place in a normal area where water baths and

- 7 -

associated equipment can be safely used. Connection of the assembly to the measurement instrument is then preferably made via a shunt-diode safety barrier.

5 Several embodiments of the invention will now be described by way of example with reference to the accompanying drawings in which:

10 Figure 1 is a schematic diagram of an indicator electrode with the calibration unit installed;

 Figure 2 is a schematic diagram of an electrode combination pair with the calibration unit installed;

15 Figure 3 is a schematic diagram of a sensor probe with the calibration unit installed in a corner unit separate from the sensors;

20 Figure 4 shows a schematic diagram of an electrode system with the calibration unit installed in a lead;

 Figure 5 is a block circuit diagram of the calibration unit; and

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Figures 6a to 6e show various known electrodes which can incorporate the invention.

Figure 1 shows an indicator electrode incorporating a calibration unit. A cylindrical glass container 1 carries at its lower end an electrode membrane 2 and encloses an electrolyte 3. The membrane 2 is connected by an electrically conducting lead 4 to a screened multi strand output lead 5. The lead 4 is screened by a metallic screening sheath 6. This is shown schematically but in practice can be located between inner and outer glass concentric walls rather than within the electrolyte 3.

The glass container 1 is carried by a carrier 7 at the top of the electrode assembly which as well as supporting the container 1 encloses wiring which feeds out into the multicore cable 5. The carrier 7 also encloses a calibration unit 8 whose output leads are connected into the multi strand cable 5.

The electrode is used in conjunction with a reference electrode, which then forms a part of the calibrated pair. The significant difference in the reference electrode is that instead of an electrode membrane 2 across which a voltage will be developed, a porous

- 9 -

5 wall is employed at its lower end so that the
reference electrode is retained at a potential derived
from the solution within the electrode and is
therefore constant. While the calibration data is
retained in the unit associated with the indicator
electrode, the calibration also takes account of
variations within the reference electrode. Therefore
a particular reference electrode always has to be
identified and used together with the same calibrated
10 indicator electrode.

Figure 2 shows a combined electrode consisting
essentially of a measuring electrode of the kind shown
in Figure 1 combined with a reference electrode
15 surrounding it.

The same reference numbers are used for the same
component features as in Figure 1 example and these
components are essentially the same. However
20 surrounding the measuring electrode is an enclosing
glass jacket 10 thus defining within an annular
compartment a reservoir for a reference solution 11.
Within the reference solution 11 is a reference
element 12, and the lower face of the circular jacket
25 10 is closed by a porous annular plug 13. Thus, the

- 10 -

reference element can be maintained at a constant potential determined by the reference solution.

This contrasts with the measuring electrode where a
5 glass membrane 2 allows a potential to develop across
that membrane in order to sense the difference in
value between the liquids on either side of the
sensing element 2 (for measurement of Ph etc). The
reference element 12 is then connected via a
10 conducting line 14 into the multi strand output cable
5.

Figure 3 shows a further arrangement. In this
arrangement, a measuring electrode 20 and a reference
15 electrode 21 (substantially of the form shown in
Figure 1) are carried out in a connecting carrier 22
which connects to the main carrier 7. The two
electrodes 20 and 21 and an earthing terminal 22 are
connected by conductors 23 via plugs and sockets 24
20 to an output amplifier 25 and thence to the multi
strand cable 5 for feeding to the instrument (not
shown).

Figure 4 shows a further form of the invention
25 where a combined electrode 31 is fed by conductors 32
via the calibration unit 8 to the instrument (not

- 11 -

shown), i.e the calibration unit is incorporated in the electrode connecting lead.

In each of these described examples, the calibration unit 8 is always associated with one or both electrodes whereby when the or each electrode is unplugged from the instrument and taken to another location, it will always have its correct calibration.

Figure 5 shows a schematic of a particular form of calibration unit. This comprises a pair of high impedance operational amplifiers 41 and 42 which are fed from the sensors via input leads at the right hand side of the Figure and thence are fed to a pair of output leads on the left hand side of Figure 5. The unit also incorporates a microprocessor with encapsulated battery and memory unit 43 fed from multi-strand cable 5 via serial line drives 44 and 45.

Thus in practice a pair of electrodes can be calibrated and the calibration stored in the memory unit 43 and the electrodes will then be available for use when plugged into other instruments at other sites.

The invention can be applied to various forms of

- 12 -

known measuring electrode. A unit of the kind shown in Figure 5 for example can readily be incorporated in the output lead or in the carrier head for the electrode.

5

Thus, Figure 6a to Figure 6e show various electrodes to which the invention may be applied. These electrodes are as follows:-

10

Figure 6a shows a metal electrode,
Figure 6b shows a coated metal electrode,
Figure 6c shows a solid state ion selective electrode,
Figure 6d shows a liquid ion exchange ion selective electrode,
Figure 6e is a pH electrode.

15

In these electrodes the components are as follows:-

20

In Figures 6a and 6b, 51 denotes the insulation and 52 is the electrode proper while in Figure 6b 53 denotes a sensing coating.

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In regard to Figure 6c, the solid state ion selective electrode, 55 denotes an electrically conductive contact for a solid membrane 54.

5 In Figure 6d, the liquid ion exchange ion selective electrode 57 is an internal reference solution 58 is an internal reference element and 56 is a sensing membrane across which a voltage can be developed.

10

 Finally, Figure 6e denotes a conventional pH electrode incorporating a glass membrane 59 and extending from a glass body 60 which encloses an internal reference element 61 within an internal
15 reference solution 62.

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CLAIMS

1. A measuring instrument which has measuring
5 sensors which require calibration, and located in
close association with said sensors a calibration unit
including a memory means which is arranged to store
calibration data to enable the assembly to be used
with more than one sensing instrument.
10
2. An instrument according to claim 1 in which the
sensors are measuring electrodes of an
electro-analytical sensing instrument.
- 15 3. An instrument according to claim 2 in which the
measuring electrodes are Ph electrodes.
4. An instrument according to any of the preceding
claims in which the sensor includes a carrier housing
20 and the calibration unit is located within said
carrier housing.

- 15 -

5. An instrument according to any of the preceding claims comprising a pair of electrodes one of which is an indicator electrode and the other is a reference electrode and said calibration unit is associated with
5 the indicator electrode.

6. An instrument according to claim 5 in which the indicator electrode and reference electrode are combined in a single unit.

10

7. An instrument according to claim 1 in which the calibration unit is carried within an output lead of the sensor.

15 8. An instrument substantially as herein described with reference to the accompanying diagrammatic drawings.

9. An electrode assembly for use in an instrument
20 according to any one of the preceding claims.

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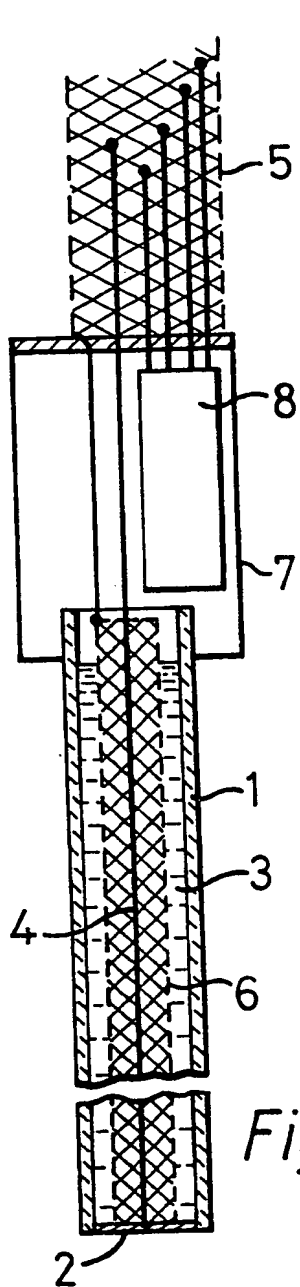


Fig. 1

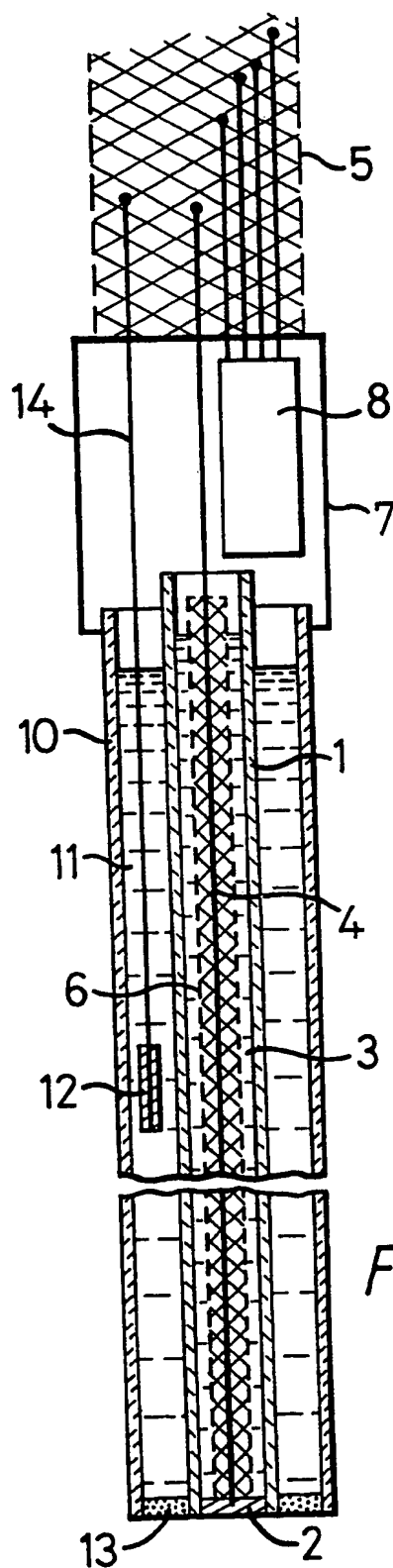
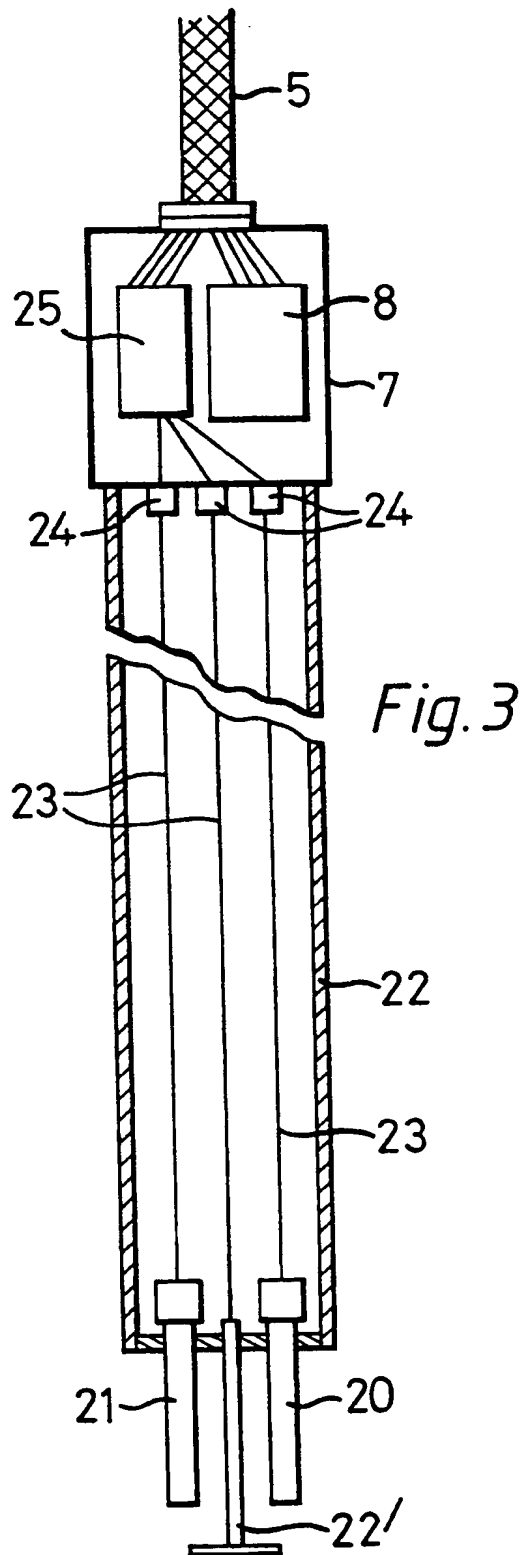


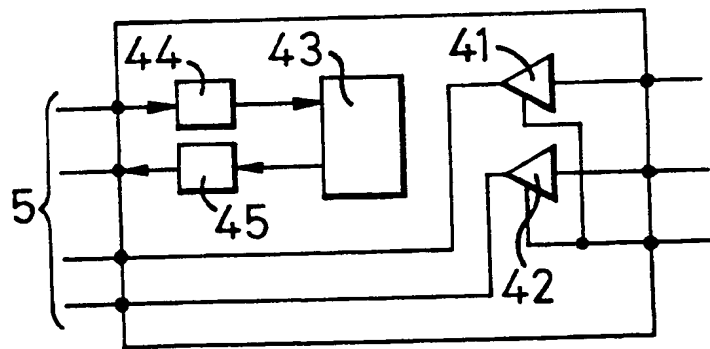
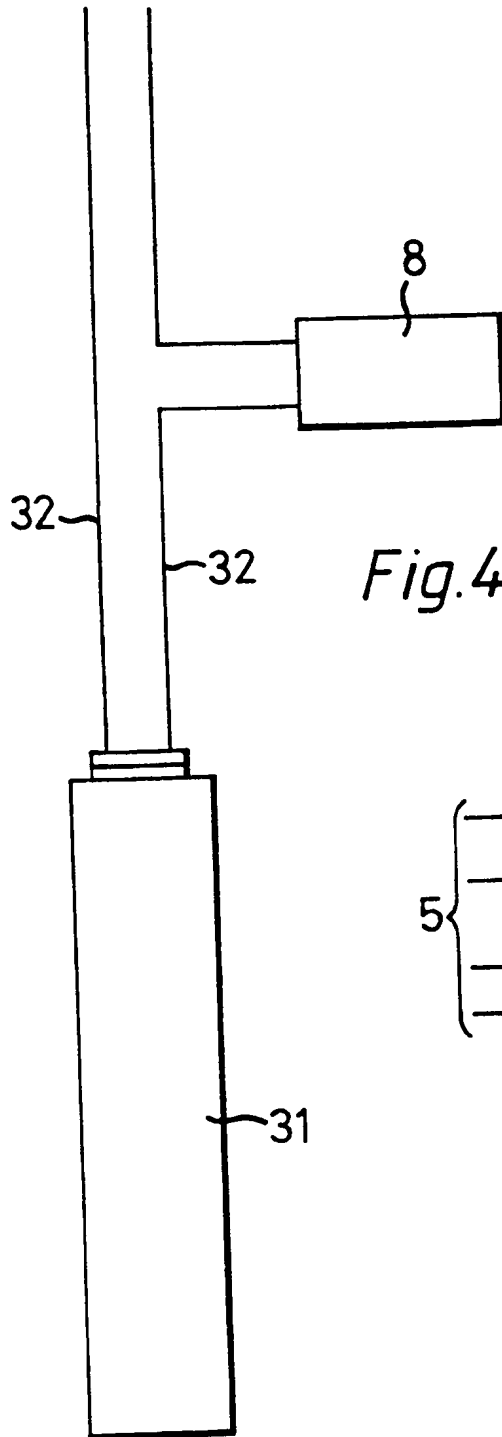
Fig. 2

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SUBSTITUTE SHEET

3/4



4/4

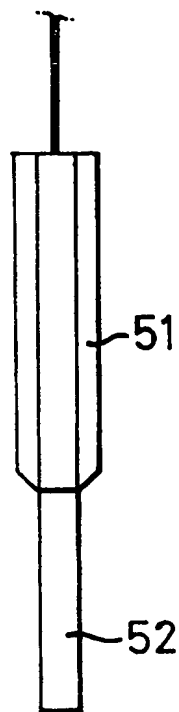


Fig. 6a

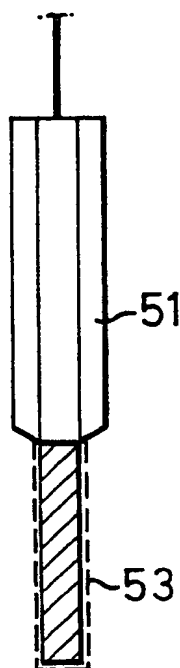


Fig. 6b

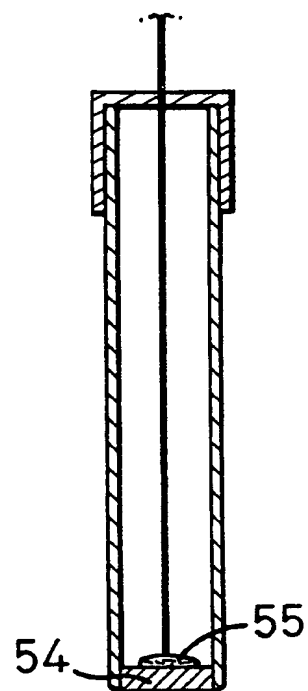


Fig. 6c

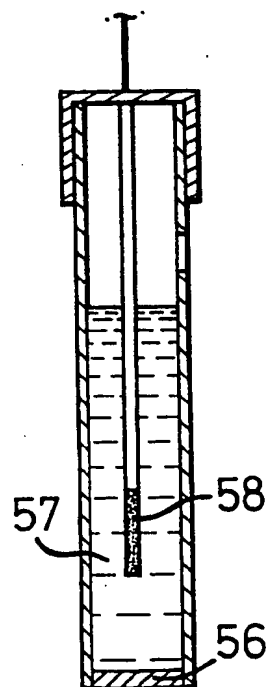


Fig. 6d

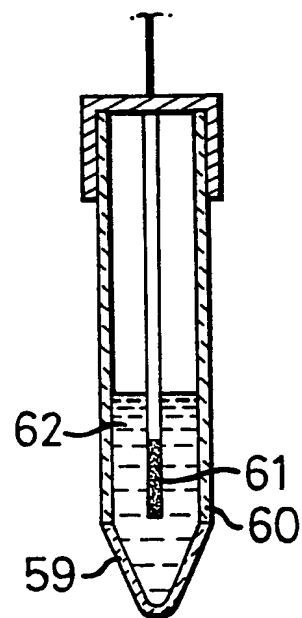


Fig. 6e

INTERNATIONAL SEARCH REPORT

PCT/EP 92/00769

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G01N27/416

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

G01N

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	DE,A,3 323 040 (W. NICOLAI) 17 January 1985 see page 7, line 30 - page 8, line 18; figure 2 ---	1
Y	EP,A,0 074 498 (W. MINDT) 23 March 1983 see page 4, line 21 - page 7, line 32; figure 2 ---	1
A	FR,A,2 354 558 (J. BOEKE) 6 January 1978 see figure 1 ---	1
A	EP,A,0 142 226 (H. SCHWARTZ) 22 May 1985 see claims 1-8 ---	1
A	DE,A,2 845 805 (F. WUESTHOFF) 26 April 1979 see figure 2 ---	1

¹⁰ Special categories of cited documents:¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance¹⁰ "E" earlier document but published on or after the international filing date¹⁰ "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)¹⁰ "O" document referring to an oral disclosure, use, exhibition or other means¹⁰ "P" document published prior to the international filing date but later than the priority date claimed¹⁰ "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹⁰ "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹⁰ "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.¹⁰ "&" document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

04 AUGUST 1992

Date of Mailing of this International Search Report

10. 08. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

DUCHATELLIER M.

m j r

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. EP 9200769
SA 58791**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-3323040	17-01-85	None	
EP-A-0074498	23-03-83	JP-A- 58050942	25-03-83
		US-A- 4481804	13-11-84
FR-A-2354558	06-01-78	US-A- 4133732	09-01-79
		CA-A- 1076206	22-04-80
		DE-A- 2726271	22-12-77
		GB-A- 1586692	25-03-81
		GB-A- 1586691	25-03-81
		JP-A- 52151092	15-12-77
		JP-B- 60013144	05-04-85
		SE-B- 433008	30-04-84
		SE-A- 7706585	11-12-77
EP-A-0142226	22-05-85	US-A- 4473458	25-09-84
		JP-A- 60071943	23-04-85
DE-A-2845805	26-04-79	JP-A- 54059199	12-05-79
		US-A- 4218746	19-08-80